



All fluorine-free lithium battery electrolytes

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HIGHLIGHTS

- LiB(CN)₄ and LiDCTA are applied in all fluorine-free PEGDME/PAN electrolytes.
- Li/LiFePO₄ cells with fluorine-free electrolytes cycle 15 times with CE ≤ 98%.
- Alternative solvents are needed to increase the electrolyte anodic stability.

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ABSTRACT

Fluorine-free lithium battery electrolytes have been prepared from lithium salts with nitrile based anions, LiB(CN)₄ or LiDCTA, dissolved in PEGDME or PC. After soaked into electrospun PAN membranes the resulting electrolytes were tested for physical and electrochemical properties and compared with reference PAN electrolytes containing LiPF₆ or LiTFSI. The fluorine-free electrolytes were successfully cycled in Li/LiFePO₄ cells at room temperature with up to 98% Coulombic efficiency. Small and qualitatively different effects were observed with the addition of Al₂O₃ particles to the PAN membranes, which could be of importance for long-term performance. However, for fluorine-free electrolytes to be truly competitive, the relatively low anodic stability and elevated temperature performance must first of all be improved by a change of solvent – or addition of co-solvents. Further work in this direction is encouraged by the strong influence of the solvent (PC or PEGDME) on the properties of the LiDCTA electrolytes demonstrated in this work.

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1. Introduction

There is an on-going paradigm shift in energy generation with new demands on energy storage solutions, such as batteries. In particular in the automotive industry, batteries are increasingly implemented to support electric propulsion to different degrees. In effect, new targets are set for battery safety, cost, and performance [1].

Li-ion batteries are facing safety challenges, being plagued by the reactivity of the highly volatile organic solvents and the use of the meta-stable LiPF₆, acting as an initiator of electrolyte decomposition [2–6]. This results in a sensitivity to high temperature operation, where degradation occurs faster, and a risk of releasing toxic [7] and bioaccumulating [8] decomposition products.

Degradation is mitigated, but not stopped, only by including a cocktail of electrolyte additives [9], which adds to the complexity and already high cost of the electrolyte [10]. Thus, there are several strong incentives to develop and evaluate alternative electrolytes beyond the state of the art, both in terms of salts and solvents. Furthermore, the advent of the Li–S and Li–air battery concepts relies on the development of new, stable electrolyte materials that can tackle the specific challenges of these technologies, such as controlling polysulphide dissolution (Li–S) [11] or resist electrolyte attack by oxygen radicals (Li–O₂) [12].

Fluorine-free electrolytes represent a promising route to improve Li-battery electrolytes in general, since electrolyte safety, stability, as well as cost are associated negatively with the use of a fluorine salt. However, it represents a challenge to find a suitable combination of salt and solvent that can fulfill the requirements of electrolyte stability and electrode compatibility [13]. Yoon et al.

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recently used the nitrile based dicyanamide (DCA^-) anion as a cost effective, low viscous, and low volatile component of ionic liquid (IL) electrolytes for Li-battery applications [14]. In addition to demonstrating 200 cycles at 80 °C in Li/LiFePO₄ cells with good capacity retention, tests also showed the electrolyte to be tolerant towards low levels of moisture, which in a conventional electrolyte with LiPF₆ would initiate electrolyte decomposition [2]. This is a most welcome result that may ease the very strict constraints of low ppm water and benefit large-scale production and overall electrolyte cost. However, compared to molecular solvents ILs are expensive, and furthermore DCA^- has a low oxidation stability (<4 V), which limits the choice of cathode.

Amongst nitrile anion alternatives, $\text{B}(\text{CN})_4^-$ and several other hypothetical anions have been predicted to be more tolerant towards oxidation than DCA^- [15]. Although $\text{LiB}(\text{CN})_4$ has a low solubility in ILs, we have previously demonstrated this salt to be successfully implemented in polyethylene glycol dimethyl ether (PEGDME) electrolytes [16]. For these solvents, LiPF₆ and similar salts were early on avoided, because of the risk of chain scission initiated by the corresponding Lewis acids (PF₅) [17]. Another nitrile salt of potential use in lithium battery electrolytes is lithium 4,5-dicyano-1,2,3-triazolate (LiDCTA) [18,19]. It was first implemented in solid poly(ethylene oxide) (PEO) electrolytes, where it showed high Li⁺ transference numbers and a strong plasticizing effect [18], and has since been investigated as a component of ILs [20] and served as model for the design of new lithium salts [21–23]. However, investigations of its use in alternative electrolytes have been far from exhausted and it may be a suitable candidate salt for PEGDME based electrolytes. PEGDME has recently been advocated as the solvent of choice for safe 2 V Li-ion batteries, for use with a TiO₂ anode and LiCoO₂ cathode, and also the low molecular weight PEGDMEs, commonly referred to as glymes, are receiving considerable attention across different battery technology platforms [24–28] – also in conceptually new high concentration lithium salt electrolytes [29].

Here we investigate electrolytes based on $\text{LiB}(\text{CN})_4$ in PEGDME and LiDCTA in PEGDME or propylene carbonate (PC), which are absorbed into highly porous polyacrylonitrile (PAN) membranes (Fig. 1). We compare the physical and electrochemical properties of these electrolytes with LiPF₆:PC and LiTFSI:PEGDME electrolytes in

PAN membranes, and address critical properties, such as the stability towards a Li anode and the anodic stability at several surfaces, including the compatibility with an Al current collector. Furthermore, by impregnating the PAN membranes with ceramic particles like Al₂O₃, we briefly investigate composite electrolytes as a possible route to enhance the performance by changing the electrolyte/electrode interface.

2. Experimental

The $\text{LiB}(\text{CN})_4$ salt was prepared by ion exchange from the corresponding *N*-butyl-*N*-methylpyrrolidinium IL ($\text{C}_4\text{mpyrB}(\text{CN})_4$, Merck High Purity) according to the procedure reported in Ref. [30]. The LiDCTA salt was synthesized in a two steps procedure. First, the acid form of 4,5-dicarbonitrile-1,2,3-triazole (HDCTA) was synthesized as follow: 62.37 g of diaminomaleonitrile (98%, Aldrich) was dissolved in 500 mL of diethyl ether placed in an ice bath. After 30 min, *tert*-butyl nitrile (90%, Aldrich) was added. After stirring for 8 h, the solution was stored at 4 °C for another 48 h. The resulting solution (containing dark solid particles) was centrifuged and the liquid phase was evaporated at 50 °C resulting in crude HDCTA (55.2 g) in the form of a brownish/reddish powder with white crystals. The HDCTA was sublimated repetitively until pure white crystals were obtained. Next, LiDCTA was obtained by reacting HDCTA with a 10% excess of Li₂CO₃ in anhydrous acetonitrile. The solution was filtered to remove solids and the acetonitrile was evaporated to give LiDCTA in the form of a white powder. The LiDCTA as obtained was dried at 80 °C under vacuum for 48 h. Commercial reference salts, LiPF₆ and LiTFSI, were obtained from Aldrich (99%). All salts were dried at 80 °C for three days prior to the electrolyte preparation, except LiPF₆ which was used as-received.

Polyethylene glycol dimethyl ether (PEGDME, $M_w = 500$, Aldrich) and PC (Aldrich, anhydrous) were used as-received to prepare 1 M electrolytes. The water level of the LiPF₆:PC and LiDCTA:PC electrolytes were determined to 30 and 50 ppm, respectively, by Karl Fischer titration (Metrohm KF Coulometer). The water content of the PEGDME electrolytes was ~700 ppm, as measured for 1 M LiTFSI:PEGDME. The higher water content relative the PC electrolytes were accepted since the nitrile and LiTFSI salts are stable in the presence of water.

Electrospun microporous polyacrylonitrile (PAN, $M_w = 150,000$, Polysciences) membranes were prepared at room temperature as reported in Ref. [31]. A 12 wt.% solution of PAN in dimethylformamide was electrospun using an electric voltage of 20 kV. A ~100 μm thin film was collected on an aluminum foil and vacuum dried at 60 °C for 12 h, before punched into circular membranes (diameter 16 mm). In addition, PAN:Al₂O₃ membranes were prepared by adding 6% Al₂O₃ (nanopowder, Aldrich) to the slurry used for electrospinning. The final electrolytes were obtained by immersing the membranes in the 1 M electrolytes for ~1 min. The PAN membrane dry weights were 5–10 mg and when soaked 80–170 mg. All materials were handled in an Ar-filled glove box with a moisture level <10 ppm.

The positive electrode was prepared by mixing the LiFePO₄ active material with carbon black (Super-P) and a poly(vinylidene fluoride) (PVdF) binder in a 80:10:10 weight ratio. The carbon coated (5 wt.%) LiFePO₄ was synthesized via a mechanical activation process reported before [32]. The components were mixed in a high-energy mill at room temperature for 30 min, using *N*-methylpyrrolidone (NMP) as a supporting solvent, to produce a homogeneous slurry cast on aluminum foil and dried under vacuum at 80 °C for 12 h to give a ~20 μm thick film. The film was cut into circular discs with a diameter of 1 cm and a mass ~2.0 mg, for subsequent use as cathodes.

Ionic conductivity measurements were performed by dielectric spectroscopy in the frequency range 100 mHz–10 MHz using a

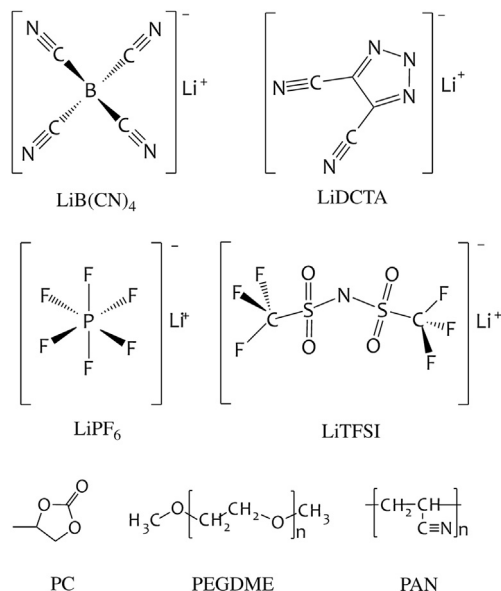


Fig. 1. Lithium salts, solvents (PC, PEGDME) and membrane (PAN) used to prepare the electrolytes in this work.

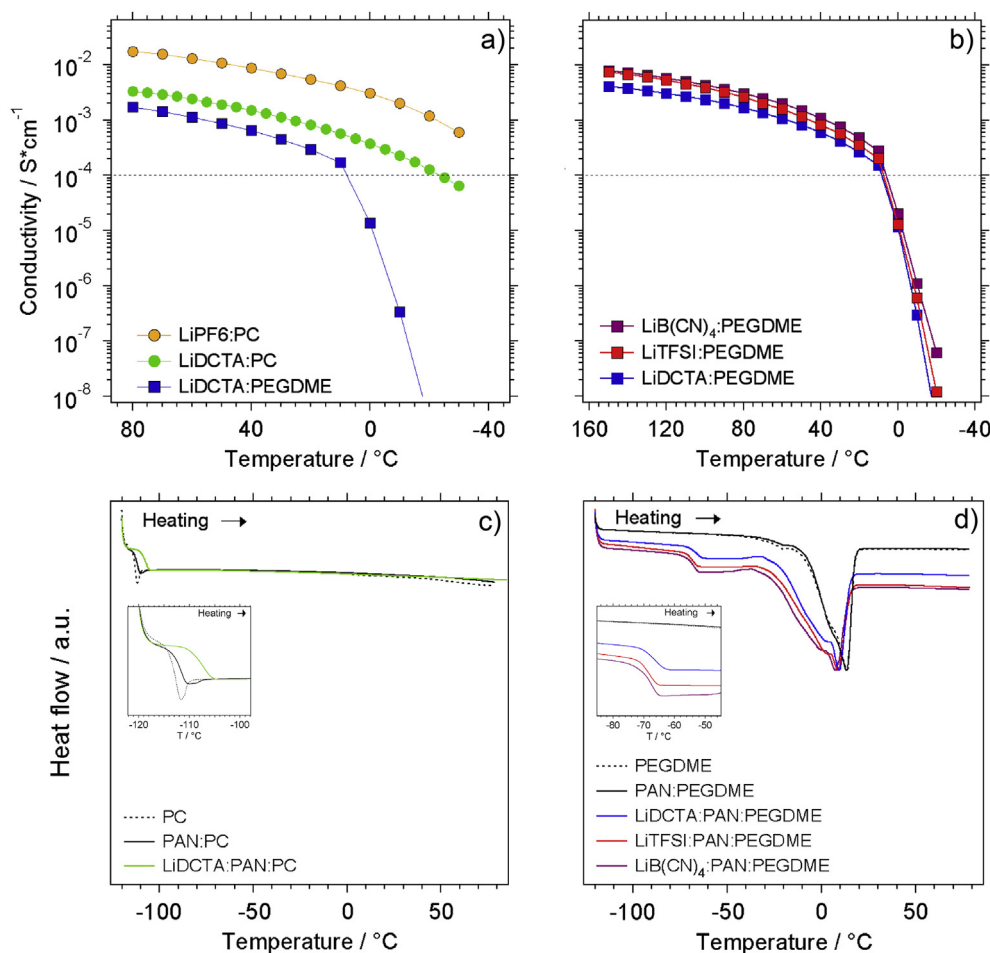


Fig. 2. a, b) Ionic conductivities of 1 M electrolytes soaked into PAN membranes. Note the different temperature ranges in a and b. c, d) DSC traces of the corresponding electrolytes. Available in colour online.

Novocontrol broadband dielectric spectrometer with a cryo-furnace. The dielectric sample cells were assembled under Ar-atmosphere by confining the electrolyte-soaked PAN membranes within a Teflon spacer (thickness 0.25 mm, with an open inner diameter of 16 mm) placed between two stainless steel electrodes. Data was collected in steps of 10 $^{\circ}\text{C}$ from -30 to 150 $^{\circ}\text{C}$ (80 $^{\circ}\text{C}$ for PC electrolytes), thermally equilibrating the cells for 15 min at each temperature before the measurements. Two full measurements were made in series to assure that the time for equilibration was adequate. In the cryo-furnace a dry sample atmosphere was maintained by a steady flow of nitrogen gas. The DC conductivity at each temperature was extracted from the low frequency plateau in the corresponding frequency vs. AC conductivity plots.

Differential scanning calorimeter (DSC) measurements were performed on samples within hermetically sealed Al pans, using a Q1000 DSC from TA instruments. The samples were first equilibrated for 3 min at 40 $^{\circ}\text{C}$, cooled to -30 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C min}^{-1}$, kept at this temperature for 3 min, then heated to 80 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$ and kept there for 3 min. Repeating the cycle, data for analysis was extracted from the second heating cycle.

The interfacial resistance between the electrolytes and a Li metal electrode was measured with electrochemical impedance spectroscopy (EIS) by analyzing the impedance response of Li/Electrolyte/Li Swagelok cells over the frequency range 100 mHz– 2 MHz, with an amplitude of 20 mV, at room temperature for 10 days (IM6 frequency analyzer). Electrochemical stability was determined by linear sweep voltammetry (LSV) of the Li/

Electrolyte/SS Swagelok cells at a scan rate of 1 mV s^{-1} , between 2 and 7 V. Cyclic voltammetry (CV) measurements of Li/Electrolyte/Al Swagelok cells were performed at a scan rate of 1 mV s^{-1} at 25 $^{\circ}\text{C}$, with five cycles between 2 and 5 V. Charge–discharge tests of the Li/Electrolyte/LiFePO₄ coin cells of type 2032 were made between 2.5 and 4.4 V at a $C/10$ current density and a temperature of 30 $^{\circ}\text{C}$ controlled by an OF-22 oven from Jeio Tech. All cells were subsequently tested at 60 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$ after equilibration for 1 h at each temperature. The electrochemical tests (LSV, CV, and charge–discharge) were carried out using an automatic galvanostatic charge–discharge unit, WBCS3000, from Wonatech.

3. Results and discussion

The electrolytes of this work were investigated both as stand-alone and in several different types of electrochemical cells. After presenting the basic physical properties, the cathodic/anodic stabilities and the cycling properties are presented, including Al current collector corrosion studies.

3.1. Physical properties

It is a challenge for any novel electrolyte to provide the very basic feature of a high concentration of charge carriers with high mobility – resulting in an acceptable ionic conductivity. Using the LiPF₆:PAN:PC electrolyte as a reference, it is evident from Fig. 2a that replacing only the salt can have a dramatic effect. Across the entire

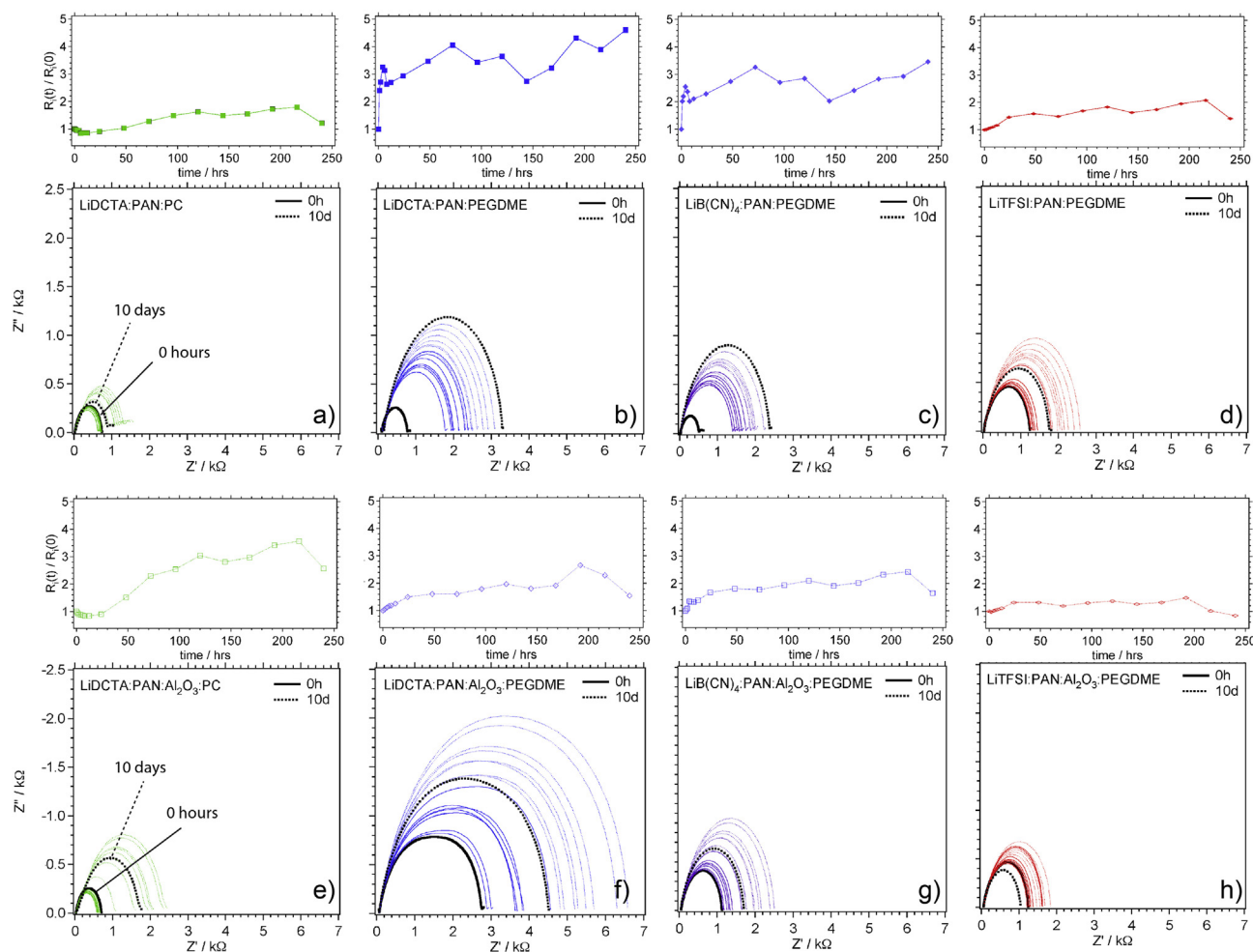


Fig. 3. a–d) Nyquist plots of PAN based electrolytes and e–h) corresponding PAN:Al₂O₃ electrolytes showing the impedance response from 0 h to 10 days. The insets show the qualitative evolution of the normalized interface resistance, $R_i(t)/R_i(0)$, ≤ 10 days. Available in colour online.

temperature range, the conductivity of a LiDCTA: PAN: PC electrolyte is nearly one order of magnitude lower. Also, by replacing PC by the more viscous PEGDME, the conductivity is decreased even further. One way to resolve this issue, and reach a conductivity comparable to LiPF₆: PAN: PC, is to increase the temperature, as indicated by the conductivities of three different PEGDME electrolytes over the extended temperature range $-40 \leq T \leq 160$ °C (Fig. 2b). For the latter electrolytes, the choice of salt has only a small, but observable, effect on the ionic conductivity. However, as indicated by the conductivity data, and seen more clearly in the DSC traces (Fig. 2c), the addition of salt, show only minor changes, with a broadening of the melting transition and the appearance of a glassy phase at approximately -70 °C, with no dependence on the type of salt. Thus, PEGDME, with its high melting point, is not a suitable alternative for a single-solvent electrolyte if sub-zero temperature battery operation is necessary [33]. Above this temperature, however, the electrolytes surpass a lower acceptable limit on ionic conductivity ($>10^{-4}$) [34]. Only at higher temperatures are the PEGDME electrolytes competitive with conventional carbonate electrolytes.

3.2. Electrochemical properties

3.2.1. Lithium metal compatibility

The electrolyte composition is known to have a large influence on the properties of the Li metal electrode/electrolyte interface [35]. From the perspective of nitrile compounds, the acidic protons

of acetonitrile and related nitrile solvents react with Li [33]. Therefore, unless stabilized, these solvents cannot generally be considered suitable. However, as recently demonstrated for an acetonitrile electrolyte [36], stabilization is possible, for example, by use of high lithium salt concentrations (>4 M). Contrary to nitrile solvents, the lack of acidic protons in several nitrile anions pose less of a problem for the corresponding salts to be used together with Li metal; DCA[−] based IL electrolytes [14], for example, sustain reversible plating and stripping of Li, and novel lithium 2-trifluoromethyl-4,5-dicyanoimidazolate (LiTDI) electrolytes have demonstrated long-term (30 day) stability in symmetric Li-cells [37] and operated successfully in Li/LiMn₂O₄ cells [23].

In the present study, symmetric Li cells with LiDCTA, LiB(CN)₄, and LiTFSI based electrolytes reveal both a solvent and salt dependence for the system impedance (Fig. 3). A qualitative analysis of the interfacial resistances, R_i , given by the diameter of the semicircles in the Nyquist plots, suggests high R_i 's and that the R_i of the PEGDME electrolytes are higher than for the PC equivalents (Fig. 3a–d). The lowest R_i over the 10 days of measurement was recorded for the LiDCTA: PAN: PC electrolyte (Fig. 3a), but the initial R_i of ~ 700 Ω is almost three times the initial value reported by Raghavan et al. for a corresponding LiPF₆: PAN: PC electrolyte [31] and much larger than for other PC based electrolytes [38]. However, differences in electrode roughness and passivation phenomena make it difficult to compare absolute values [21], which is why we focus on the qualitative and relative results.

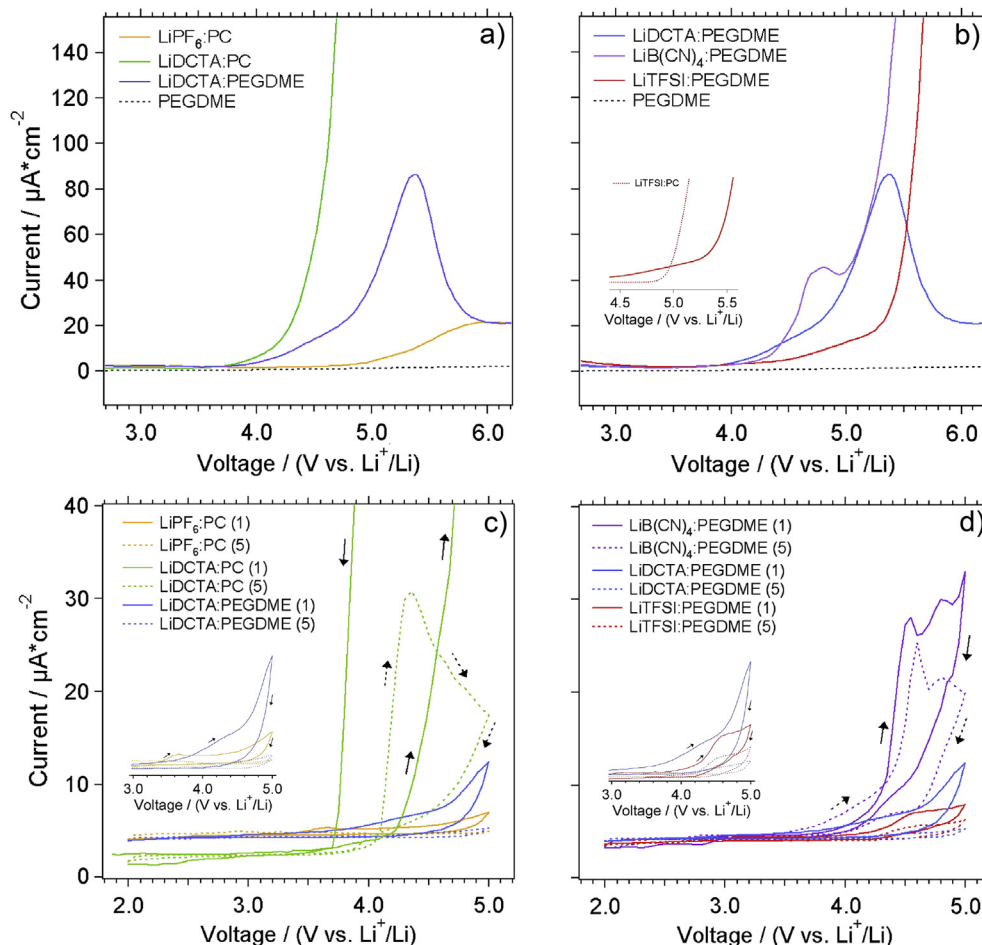


Fig. 4. a, b) LSV voltammograms of Li/SS cells with PAN electrolytes and c, d) CV voltammograms (1st and 5th cycle) of corresponding Li/Al cells. The inset of b) highlights the difference of LiTFSI:PC and LiTFSI:PEGDME electrolytes. The insets of c) and d) are magnifications of the main CV curves. Available in colour online.

The R_i of the LiDCTA: PAN: PC cell did, however, not reach a steady-state value and increased uniformly – as observed from the R_i normalized by the value at $t = 0$ (Fig. 3a). With PEGDME in place of PC, the relative increase of R_i was much more rapid and the fluctuations larger (Fig. 3b), demonstrating a clear solvent dependence. By changing the salt of the PEGDME electrolyte, to $\text{LiB}(\text{CN})_4$ (Fig. 3c) or LiTFSI (Fig. 3d) R_i was reduced, indicating also a salt dependence. Similar to the PC based electrolyte, no steady-state R_i was observed for any of the PEGDME electrolytes, but other PEGDME electrolytes have demonstrated a stable interface only after >10 days [25]. Thus, the present data does not exclude the possibility of the interfacial resistance approaching a steady-state value after even longer storage times.

Another attempt to alter the interfacial properties was made by using a PAN membrane impregnated with Al_2O_3 particles (Fig. 3e–h). Al_2O_3 particles have previously been shown to improve the solid electrolyte interphases (SEI) on Li anodes for $\text{LiAsF}_6:\text{PC}$ and $\text{LiClO}_4:\text{PC}$ electrolytes by promoting PC decomposition with generation of CO_2 (g), resulting in a higher content of Li_2CO_3 in the SEI [39]. Here the effect of the added Al_2O_3 varies with the electrolyte salt used. A negative effect on R_i is observed for the cells with a LiDCTA based electrolyte – irrespective of solvent (Fig. 3e,f). However, the cell with the $\text{LiB}(\text{CN})_4$ based electrolyte seems unaffected at large (Fig. 3g), while the interfacial resistance of the cell with LiTFSI is somewhat reduced (Fig. 3h). Thus, contrary to the physical properties of the electrolytes (ionic conductivity and liquid

temperature range), which are not influenced by the presence of Al_2O_3 (not shown), the impregnation with Al_2O_3 affects the electrochemical properties.

3.2.2. Anodic stability

Anodic stability is a bottleneck for the application of new lithium salts in Li-batteries, since conventional Li-salts with fluoro based anions, such as PF_6^- and BF_4^- , have been difficult to replace without a trade-off in anodic stability [40].

Previously, some of us have used quantum chemistry calculations to categorize the anodic stabilities of isolated anions based on anion structure and functional group, and identified several lithium fluoro-, fluoroalkyl-, or nitrile salts of interest for electrolyte application [15]. However, in reality, both the surrounding solvent and concentration of Li^+ influence the anion stability [41,42]. Furthermore, the anion can partake in solvent decomposition [43] or be catalytically decomposed on an active electrode surface, in reactions that are difficult to predict *a priori* and may change the relative stability of anions between systems [42]. Therefore, the herein experimentally determined electrolyte anodic stabilities, measured in both Li/SS and Li/Al cells (Fig. 4), should be considered only as guides to the stabilities in cells with active electrode materials.

Comparing LiDCTA: PAN: PC with the $\text{LiPF}_6:\text{PAN}:\text{PC}$ reference (Fig. 4a) shows that the aromatic anion of the former electrolyte limits the anodic stability – in accordance with calculated

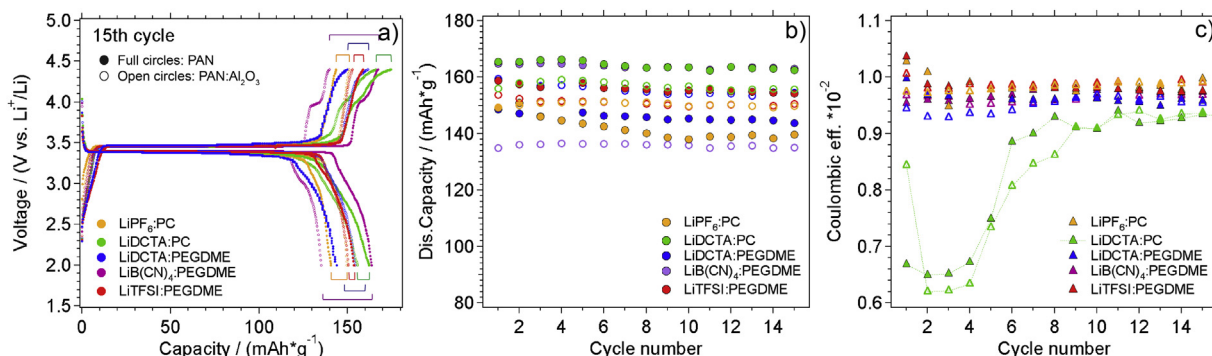


Fig. 5. a) Charge/discharge curves of Li/LiFePO₄ cells with PAN electrolytes (C/10, 2.5–4.4 V vs. Li⁺/Li, $T = 30^\circ\text{C}$), b) corresponding discharge capacities, and c) Coulombic efficiencies. Available in colour online.

predictions [22]. An oxidation current starts to flow at <4 V vs. Li⁺/Li for cells with LiDCTA electrolytes, either with PC or PEGDME, which is ~ 1 V lower than the onset of current for the LiPF₆:PAN:PC electrolyte. A more rapid increase in current is observed with LiDCTA in PC as compared to PEGDME (Fig. 4a), which is a behavior evident also for LiTFSI in PC and PEGDME electrolytes (inset Fig. 4b). However, contrary to the LiDCTA electrolytes, the onset of oxidation with LiTFSI occurs at a lower potential in PEGDME compared to PC, as PEGDME is less stable than TFSI⁻. The oxidation behavior recorded for the LiTFSI: PAN:PEGDME based cell is very similar to that observed for LiTFSI in low molecular weight glymes at ≤ 1 M salt concentration [44].

Comparing all three PEGDME based electrolytes (Fig. 4b), the onset cell potential for oxidation is similar, but the current develops differently at slightly higher potentials. Possibly a simultaneous oxidation of PEGDME and the anion is responsible for the higher currents observed in the nitrile based electrolytes as compared to the LiTFSI reference electrolyte. At ~ 4.5 V vs. Li⁺/Li there is a prepeak to the main oxidation event in the voltammogram of LiB(CN)₄ which has been observed before [16], but its origin was not identified. However, when a LiB(CN)₄:PEGDME electrolyte was applied as the electrolyte in a Li-air cell (charged to 4.5 V vs. Li⁺/Li), several boron species were identified on the cathode surface by XPS, and the origin of these species was ascribed to electrochemical decomposition [30]. Thus, it is possible that the prepeak in the cell with LiB(CN)₄:PAN:PEGDME is due to a combination of solvent and anion decomposition.

With LiDCTA: PAN:PEGDME as the electrolyte, the oxidation current goes through a weaker maximum. This behavior is somewhat surprising, since DCTA⁻ is readily oxidized in the PC electrolyte. The result was repeated in several cells and accompanied by the formation of a clearly observable yellow deposit on the membrane surface, which suggests that the decomposition products may block fresh electrolyte from accessing the cathode surface and thereby limit the oxidation current.

3.2.3. Aluminum corrosion

A second process that relates to the anodic stability of the electrolyte is the corrosion of Al which is used as current collector for the positive electrode of Li-batteries. Al corrosion is an important phenomenon, being only kinetically stable at potentials >1.4 V vs. Li⁺/Li due to the naturally occurring passivation film on the surface [45]. If this film is damaged during manufacturing, or battery operation, the electrolyte needs to be able to re-passivate the current collector, which otherwise would be continuously corroded. Al corrosion is a well-documented problem for LiTFSI and related salts in carbonate electrolytes [45–48].

In Fig. 4, LSV data for Li/SS cells (a, b) and the corresponding CVs for Li/Al cells, first and fifth cycle (c, d), are shown. The relative distribution of maximum currents is the same in the Li/Al cell configuration – the maximum current is observed for the cell with the LiDCTA: PAN:PC electrolyte and the minimum current for the cell with the LiPF₆ electrolyte. The LiPF₆: PAN:PC results compare well to previous studies [45,48,49], where a small current developing only at the first anodic scan, here at 3.2 V vs. Li⁺/Li, is indicative of a passivation film formed on the Al surface (preventing further reactions at this potential during subsequent cycles).

For the LiDCTA: PAN:PC electrolyte, a much stronger oxidation current is observed at >4 V vs. Li⁺/Li in the first CV scan. The hysteresis loop observed on the cathodic scan is a signature of Al corrosion [45]. However, the strong decrease in current by the fifth cycle indicates that some passivation occurs, but does not prevent oxidation altogether at potentials ≥ 4.1 V vs. Li⁺/Li. With a change of solvent from PC to PEGDME, the passivation seems to be much improved and resembles the CV for the LiPF₆: PAN:PC reference electrolyte. The LiTFSI: PAN:PEGDME cell behaves similarly (Fig. 4d), as expected from results reported elsewhere [45], but the difference between the first and fifth cycles is not as clear as with LiDCTA: PAN:PEGDME. The cell with the LiB(CN)₄: PAN:PEGDME electrolyte performs worst. Oxidation currents are strong both at the first and fifth cycles and the onset for oxidation moves to lower potentials with increasing cycle number. Overall, both the choice of salt and solvent are important factors to enable a passivation of the Al surface. With PEGDME as the solvent, LiDCTA seems to be a better choice than LiB(CN)₄. However, as both nitrile based salts demonstrate an anodic stability inferior to LiTFSI, unless improved by synergistic effects in alternative solvents or in the presence of an active cathode material, their possible use will be limited to batteries working below ~ 4 V vs. Li⁺/Li.

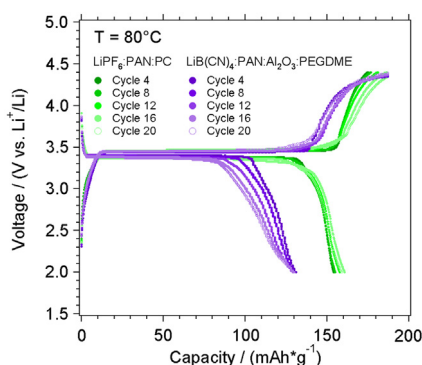
3.2.4. Cell cycling tests

The electrolytes were further proof-of-concept tested in Li/LiFePO₄ coin cells over a short series of 15 charge/discharge cycles (Fig. 5). As evident from Fig. 5a, there were large variations in discharge capacities among the individual cells, but the focus here is on qualitative cell performance rather than absolute capacities.

Despite the high charge cutoff at 4.4 V vs. Li⁺/Li, deliberately chosen to challenge the cells with the nitrile based electrolytes, all of the cells demonstrated a stable discharge capacity over 15 cycles (Fig. 5b, Table 1). More notable was the Coulombic efficiencies (CE) as a function of electrolyte (Fig. 5c), as most cells demonstrated little or no decrease in CE for the first few cycles, quickly reaching stable values $\geq 96\%$. However, the cells with the LiDCTA: PC electrolyte demonstrated very low efficiencies for the first four cycles,

Table 1Average Coulombic efficiencies (CE) of Li/Electrolyte/LiFePO₄ cells (cycle 11–15).

Electrolyte	Coulomb. eff.
LiTFSI:(PAN:Al ₂ O ₃):PEGDME	99%
LiPF ₆ :(PAN:Al ₂ O ₃):PC	99%
LiPF ₆ :PAN:PC	99%
LiTFSI:PAN:PEGDME	98%
LiB(CN) ₄ :PAN:PEGDME	98%
LiB(CN) ₄ :(PAN:Al ₂ O ₃):PEGDME	97%
LiDCTA:(PAN:Al ₂ O ₃):PC	96%
LiDCTA:PAN:PEGDME	96%
LiDCTA:(PAN:Al ₂ O ₃):PC	93%
LiDCTA:PAN:PC	93%

**Fig. 6.** Charge/discharge curves of Li/LiFePO₄ cells at $T = 80\text{ }^{\circ}\text{C}$ (C/10, 2.5–4.4 V vs. Li⁺/Li). Available in colour online.

60–70%, but reached a stable CE $\geq 90\%$ after approximately ten cycles. Taken together with the anodic stability tests, the cells with LiDCTA clearly suffer from the low anodic stability of DCTA[−]. However, the choice of solvent is obviously very important, since the cell performance is much improved when PC is replaced by PEGDME. From these cell tests, the effect of including Al₂O₃ is negligible for the performance over the limited number of cycles in this work.

Each cell in the charge–discharge tests were further tested at 60 °C and 80 °C to possibly make use of the higher ionic conductivity of the electrolytes, and to explore the stability of the cells at elevated temperatures. However, most cells were rapidly degraded when cycled at 60 °C (not shown). Only two cells survived cycling at 80 °C; the LiPF₆:PAN:PC and the LiB(CN)₄:PAN:Al₂O₃:PEGDME electrolyte based (Fig. 6), but at a severe expense of performance. The cell with the LiB(CN)₄ based electrolyte, showed a CE of only 70% by the 16th cycle and the cell with a conventional LiPF₆ based electrolyte 86% CE, both to be compared with CEs of ~ 97 –99% at 30 °C (Fig. 5c). This is in contrast to the promising high temperature results of Yoon et al. using their fluorine-free IL electrolytes with LiDCA [14]. However, the much higher voltage cutoff used in this work (4.4 V vs. 3.6 V) represents more severe conditions, where PEGDME is not stable enough to avoid electrolyte degradation.

4. Conclusions

Fluorine-free electrolytes were prepared from two different lithium nitrile salts, LiB(CN)₄ and LiDCTA, dissolved in PEGDME and soaked in PAN membranes. The basic physical properties reveal that the choice of PEGDME as a solvent restricts the useful temperature range for such electrolytes to $T > 0\text{ }^{\circ}\text{C}$. The conductivities of the PEGDME electrolytes vary little as a function of lithium salt, but there is a small advantage for LiB(CN)₄ over LiDCTA. With a

conductivity of 0.5 mS cm^{-1} at 20 °C, these electrolytes trail conventional carbonate based electrolytes by an order of magnitude and the conductivity becomes competitive only at elevated temperatures. At 80 °C the conductivity of LiB(CN)₄:PAN:PEGDME is appreciable 3 mS cm^{-1} , but at this temperature battery cell operation is challenging.

At room temperature the situation is different, where it is possible to cycle Li/LiFePO₄ cells with all of the electrolytes investigated in this work. However, differences in anodic stability and in the ability to passivate the electrode surfaces result in different Coulombic efficiencies. Al₂O₃ particles added to the PAN membrane revealed only small, but qualitatively different, effects on the cell level, which can be of importance for long-term performance. Of the fluorine-free electrolytes in this work, a reference LiDCTA:–PAN:PC electrolyte is clearly the worst performing, but the effect of the solvent is strong and cell performance is much improved with PEGDME as the solvent. The performance of the Li/LiFePO₄ cells with LiB(CN)₄ or LiDCTA in PEGDME are quite comparable. However, to make full use of the fluorine-free salts, alternative salt and solvent combinations have to be researched for improved ionic conductivities and possible synergy effects – to be truly competitive.

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